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VIBRATIONAL DISTRIBUTION FUNCTIONS IN  
ANHARMONIC OSCILLATORS

G.E. Caledonia and R.E. Carter

RESEARCH REPORT 364

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AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

Kirtland Air Force Base, New Mexico

and

ADVANCED RESEARCH PROJECTS AGENCY

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by

G. E. Caledonia and R. E. Center

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Everett, Massachusetts

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## ABSTRACT

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## I. INTRODUCTION

The process of vibrational relaxation under nonequilibrium conditions, such that the vibration mode is out of equilibrium with the other degrees of freedom, is of considerable importance in many physical phenomena. The upper atmosphere provides an example wherein the nitrogen vibrational energy is thought to be determined by collisions with free electrons and metastable oxygen atoms and is out of equilibrium with the low translational temperature. A similar situation arises in expanding gas flows, molecular lasers, and many chemical reactions where the vibrational temperature may be much higher than the translational temperature. In the past, analyses of such nonequilibrium conditions have been characterized by a Boltzmann distribution corresponding to a specific temperature for each degree of freedom. Recently, several theoretical analyses have been developed to avoid the restriction of a Boltzmann distribution in the vibrational mode.<sup>1,2</sup>

There are two basic collisional phenomena in the relaxation of a diatomic molecular gas from a state of vibrational nonequilibrium. These are the processes of vibration-vibration, V-V, and vibration to translation, V-T, energy exchange. In the following analysis we will assume that the translational and rotational degrees of freedom are in equilibrium so that vibration-rotation, V-R, or vibration-rotation-translation, V-R-T, energy exchange processes are indistinguishable from V-T processes. In general, the V-V relaxation rates are much faster than the V-T rates,

and under suitable conditions a gas may relax to a state of vibrational quasi equilibrium before V-T processes become important. The collisional exchanges may occur between different species, intermode exchange, or between different vibrational levels of the same species, intramode exchange. For an anharmonic oscillator the intramode exchange may be the controlling mechanism in the relaxation process.

Treanor et al<sup>1</sup> have considered the relaxation behavior of anharmonic oscillators when the vibrational mode is out of equilibrium with the translational mode under conditions of V-V equilibrium with no quantum loss mechanism. For these conditions they deduced non-Boltzmann distributions in the anharmonic oscillator with the vibrational energy pumped to the closely spaced upper vibrational levels. These theoretical distributions are unrealistic in the higher levels in that they neglect energy loss processes which prevent large accumulation of energy in these levels. Bray<sup>2</sup> has treated the relaxation process allowing for V-T energy exchange and has obtained numerical results for quasi steady state distributions in a single species. In these calculations the loss of vibrational energy via V-T processes prevents the large total inversions predicted by Treanor et al. These analyses of Treanor and Bray did not include the effects of radiative decay which can be important in low pressure systems where the effective time between energy exchange collisions becomes comparable with the radiative lifetime. Some preliminary calculations have shown that the radiative decay may be the dominant loss mechanism in the  $N_2$ -CO mixing laser.<sup>3</sup>



The present paper describes steady state solutions for conditions of vibrational nonequilibrium in gas systems composed of diatomic molecules. Both radiative decay and V-T collisional exchange are included in the analysis which is applied to pure CO and  $N_2$ -CO mixtures. Vibrational distribution functions are derived for a variety of conditions, and comparisons are made with existing experimental data in the electrically excited  $N_2$ -CO system.

## II. KINETICS

Consider a mixture of two diatomic molecular gases N and M. We assume that only single quantum transitions occur in the collisional exchange processes of vibration-vibration (V-V) and vibration-translation (V-T) as well as in the radiative decay. The intramolecular, intermolecular and radiative processes for species N are



where the vibrational level is denoted by subscripts v, v', and v''. A similar set of reactions applies to species M. One can write the master vibrational rate equation for the density of molecule N in the  $v^{\text{th}}$  vibrational level

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$$\begin{aligned}
\frac{dN_v}{dt} = & Z_{N-N} \sum_{v'} \left\{ P_{v',v'-1}^{v-1,v} N_{v-1} + P_{v',v'+1}^{v+1,v} N_{v+1} - \left( P_{v',v'+1}^{v,v-1} + P_{v',v'-1}^{v,v+1} \right) N_v \right\} N_{v'} \\
& + Z_{N-M} \sum_{v''} \left\{ P_{v'',v''-1}^{v-1,v} N_{v-1} + P_{v'',v''+1}^{v+1,v} N_{v+1} - \left( P_{v'',v''+1}^{v,v-1} + P_{v'',v''-1}^{v,v+1} \right) N_v \right\} M_{v''} \\
& + Z_{N-N} \left\{ P_{V-T'}^{v-1,v} N_{v-1} + P_{V-T'}^{v+1,v} N_{v+1} - \left( P_{V-T'}^{v,v-1} + P_{V-T'}^{v,v+1} \right) N_v \right\} \sum_{v'} N_{v'} \\
& + Z_{N-M} \left\{ P_{V-T''}^{v-1,v} N_{v-1} + P_{V-T''}^{v+1,v} N_{v+1} - \left( P_{V-T''}^{v,v-1} + P_{V-T''}^{v,v+1} \right) N_v \right\} \sum_{v''} M_{v''} \\
& + N_{v+1}/\tau_{v+1} - N_v/\tau_v
\end{aligned} \tag{6}$$

where  $Z_{N-N}$  and  $Z_{N-M}$  are the gas kinetic collision frequencies of species N colliding with species N and M respectively, at unit concentrations.

The probabilities  $P_{v',v'+1}^{v,v-1}$  and  $P_{V-T'}^{v,v+1}$  refer to the V-V and V-T exchange

respectively and  $\tau_v$  is the radiative lifetime of level v. The forward and reverse rate constants are related through detailed balancing and for a Maxwellian velocity distribution corresponding to the translational

temperature T' we obtain:

$$P_{v',v'-1}^{v,v+1} = P_{v'-1,v'}^{v+1,v} \exp. \left( \left[ (E_{v'} - E_{v'-1}) + (E_v - E_{v+1}) \right] / kT \right) \tag{7}$$

$E_v$  is the energy of the  $v^{\text{th}}$  vibrational level which is approximately

$$E_v = \left[ (v + \frac{1}{2}) \omega_e - (v + \frac{1}{2})^2 \omega_e x_e \right] hc \quad (8)$$

and the molecular constants  $\omega_e$  and  $\omega_e x_e$  are given in Ref. 4.

The time rate of change of vibrational energy can be obtained by multiplying the "master equation" (6) by  $v$  and summing over all values of  $v$ . In the case of harmonic oscillators, the energy relaxation equation is considerably simplified. For a mixture of gases N and M it can be shown that

$$\begin{aligned} \frac{dE_N}{dt} = & \frac{\bar{E}_N - E_N}{\tau_{V-T}} - \frac{E_N}{\tau_{\text{rad}}} \\ & + \frac{\psi_M e^{\Theta_M/T}}{k \tau_{V-V} \Theta_M} \left\{ E_M (\bar{E}_N - E_N) (1 - e^{-\Theta_N/T}) - E_N (\bar{E}_M - E_M) (1 - e^{-\Theta_N/T}) \right\} \end{aligned} \quad (9)$$

with a similar equation for species M where use has been made of the Landau-Teller selection rules.<sup>5</sup> Here  $\psi_M$  is the mole fraction of species M,  $E$  is the vibrational energy per molecule,  $\bar{E}$  is the equilibrium vibrational energy at the translational temperature  $T$ , and  $\Theta$  is the characteristic vibrational temperature, i. e.  $(E_1 - E_0)/k$ .  $\tau_{V-T}$  and  $\tau_{V-V}$  are the vibrational relaxation times for V-T and V-V processes. For times  $t$  such that  $\tau_{V-V} \ll t \ll \tau_{V-T}$ ,  $\tau_{\text{rad}}$  a quasi equilibrium of the V-V process is obtained. The bracketed expression in the above equation is then zero so that

$$\frac{\Theta_N}{T_{VN}} - \frac{\Theta_M}{T_{VM}} = \frac{\Theta_N - \Theta_M}{T} \quad (10)$$

where  $T_{VN}$  and  $T_{VM}$  are the vibrational temperatures of species N and M respectively. It is clear that these temperatures must be different under conditions of thermal nonequilibrium and for  $T < T_{VN}$ ,  $T_{VM}$  the species with the lower characteristic temperature will have the higher vibrational temperature. This has been previously derived by Teare<sup>6</sup> and independently by Treanor.<sup>7</sup> In the latter analysis, Treanor obtained an analytic solution to the master equations for anharmonic oscillators allowing only V-V exchanges. Their analysis exhibits a similar pumping phenomenon between different levels in the oscillator.

In the present paper, steady state solutions to the master equations are obtained numerically for conditions of thermal nonequilibrium. The equations considered are restricted to a finite number of vibrational levels whose energy cannot exceed the dissociation limit. The vibrational distribution in species N is determined by supplying a fixed source which communicates with all vibrational levels. Under many situations it is sufficient to specify a fixed temperature between the first two vibrational levels of species N. This is equivalent to the inclusion of a source term which only communicates with the first and zeroth levels. Under these conditions, the master equations may be written in the form

$$\frac{dN_0}{dt} = -F_{0,1} + D_1 - K \quad (11)$$

$$\frac{dN_1}{dt} = F_{0,1} - F_{1,2} - D_1 + D_2 + K$$

where  $K$  is the net rate of quanta supplied by the source. In these equations  $F_{v,v+1}$  is the particle flux between levels  $v$  and  $v+1$

$$F_{v,v+1} = Z \sum_i \left( P_{i,i-1}^{v,v+1} N_v N_{i-1} - P_{i-1,i}^{v+1,v} N_{v+1} N_{i-1} \right) \quad (12)$$

and  $D_{v+1}$  is the net quanta loss between levels  $v+1$  and  $v$

$$D_{v+1} = Z \left[ P_{v-T}^{v+1,v} N_{v+1} - P_{v-T}^{v,v+1} N_v \right] + N_{v+1}/\tau_{v+1} \quad (13)$$

These equations in combination with the remaining master equations yield the steady state identities

$$v \geq 1 \quad F_{v,v+1} = D_{v+1} \quad (14)$$

and it is clear that

$$K = \sum_{v=0} D_{v+1} \quad (15)$$

We assume a reflecting boundary so that there is no transport of quanta beyond the last level.

The numerical solutions to the master equations depend upon the choice of rate constants. This is in contrast to the case of pure V-V equilibrium treated by Treanor et al<sup>1</sup> in which the vibrational distribution is determined solely by detailed balancing. Unfortunately, there are few experimental data on the rate constants for V-V and V-T collisional exchange, particularly in the high vibrational levels, and one must rely on theoretical calculations. Since we are interested in comparisons of the

distribution function calculations with measurements in  $N_2$ -CO mixtures, we have restricted ourselves to collisional exchange probabilities for those gases. The probability distributions used for CO are shown in Fig. 1. The V-T probabilities were derived from experimental measurements by Millikan and White<sup>8</sup> for the  $1 \rightarrow 0$  transition and were applied to all levels using a correction for anharmonicity based on the S. S. H. model.<sup>9</sup> This model predicts that the probability varies approximately as  $\exp(\text{const. } \Delta E^{2/3})$  where  $\Delta E$  is the energy spacing between the adjacent vibrational levels.

For the probability of intramolecular V-V exchange in CO, a combination of two theoretical models was used. The first, developed by Sharma and Brau,<sup>10</sup> used a long range attractive dipole-dipole potential which is important in the exchange probability in near resonant collisions. The second, due to Rapp,<sup>11</sup> employed a short range repulsive potential for the nonresonant collisions.

Because of the large nonresonance in the first levels of  $N_2$  and CO,  $188 \text{ cm}^{-1}$ , only the short range calculation was used with an assumed steric factor of  $1/3$ . During the course of this work, some experimental data for the V-V deactivation of CO in vibrational levels 4 to 13 were obtained by Hancock and Smith<sup>12</sup> in a fluorescence experiment. The intramolecular data for CO agree to better than a factor of 2 with our theoretical estimates as shown in Fig. 1. Hancock and Smith also observed deactivation of CO by  $N_2$ <sup>13</sup> and an extrapolation of their experimental probabilities would be less than a factor of two lower than our assumed value. This is in reasonable agreement with other recent

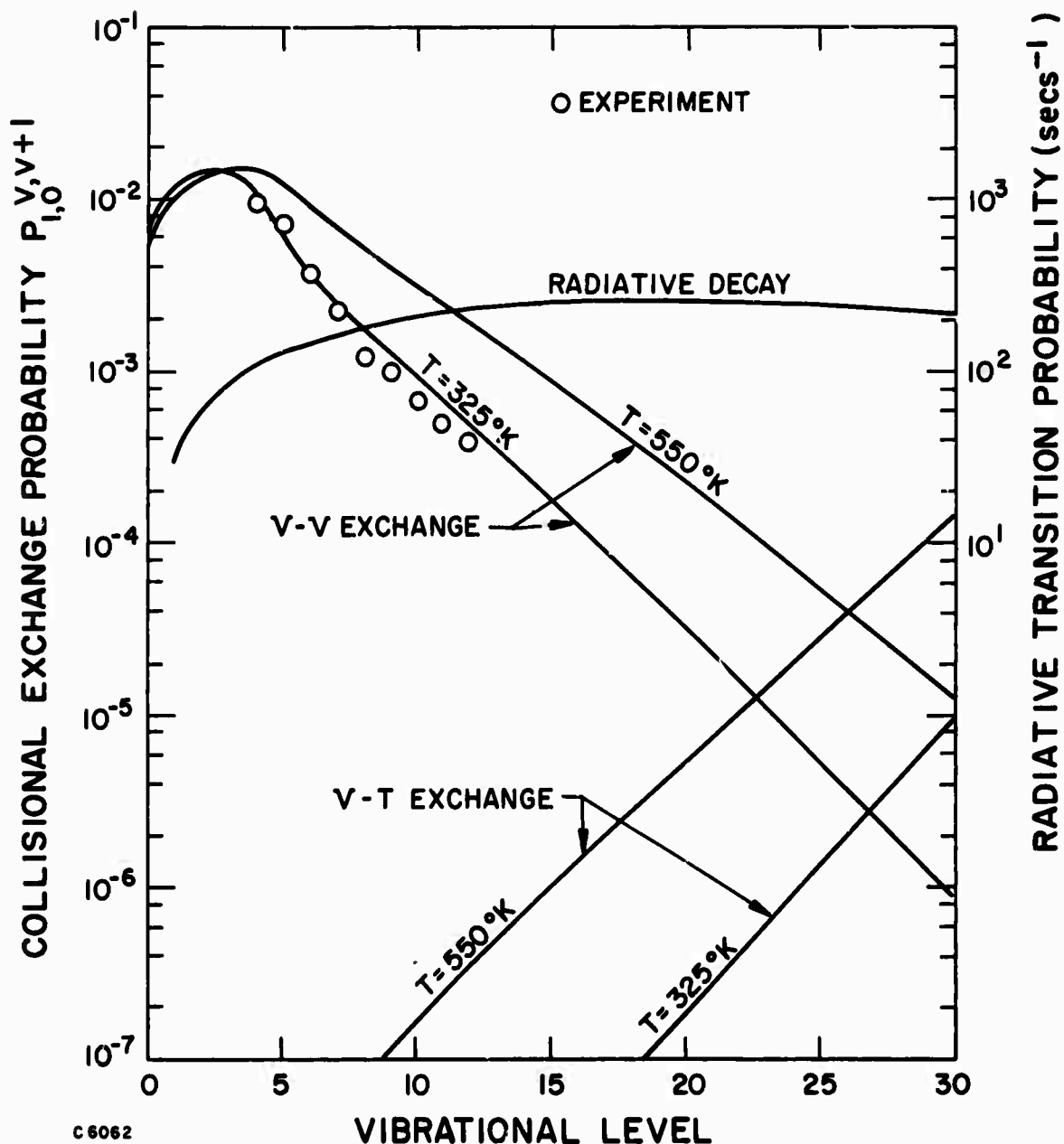


Fig. 1 Collisional exchange probabilities for both V-V and V-T processes in CO at two translational temperatures. The data points are experimental measurements of Ref. 12. Also shown is the radiative transition probability for CO.



measurements.<sup>14, 15</sup> Also shown in Fig. 1 is the radiative transition probability for CO. These values are based on the measured  $v=1$  to 0 probability and the matrix element calculation of Young and Eachus.<sup>16</sup> The variation  $\tau_v \propto v (E_v - E_{v-1})^{-3}$  is a close approximation to their calculations for both a linear and a cubic dipole moment.

### III. RESULTS AND DISCUSSION

In this section we present detailed numerical calculations for steady state distributions over a wide range of energy deactivation conditions. Results are first presented for vibrational distribution in pure CO and then for N<sub>2</sub>-CO mixtures, and finally comparison is made with experimental data in N<sub>2</sub>-CO experiments. In most cases, the vibrational temperature of the lowest levels, which we designate by  $\Theta_1^* = (E_1 - E_0) / (k \ln N_0 / N_1)$  was chosen to be 2700°K. This value is typical of the experimental conditions.

#### A. V-T Deactivation in Pure CO

The fundamental characteristics of distribution functions derived in the absence of radiative decay are of interest not only in high pressure CO, where the effects of radiative loss are negligible, but also are representative of solutions for homonuclear molecules in general.

Several vibrational distributions are shown in Fig. 2 for a value of  $\Theta_1^*$  of 2700°K. The different curves were calculated for the V-V probability distribution described in the previous section but with a variation of  $10^{-2}$  in the magnitude of the V-T probability distribution. Also shown for comparison is the Treanor solution to the master equation for V-V equilibrium without deactivation. This latter result depends solely on detailed balancing and is described by<sup>1</sup>

$$\frac{N_v}{N_{v+1}} = \exp \left( \frac{E_1 - E_0}{k\Theta_1^*} - 2v \omega_e x_e \frac{hc}{kT} \right) \quad (16)$$

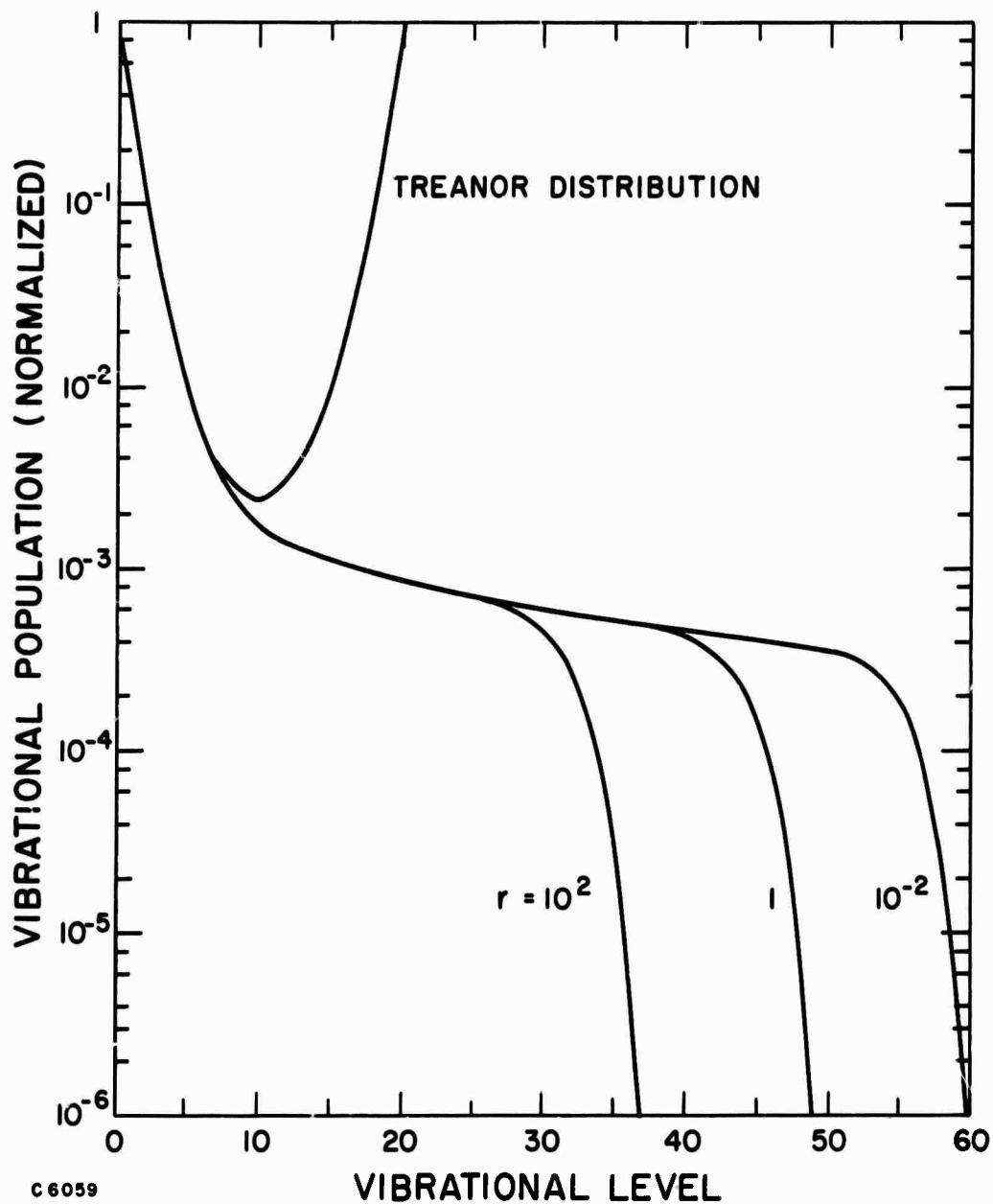


Fig. 2 CO vibrational distribution functions, neglecting radiative decay, for  $\Theta_1^* = 2700^\circ\text{K}$  and  $T = 325^\circ\text{K}$  for various values of the parameter  $r$ , the ratio of the V-T probability used in the calculation to that shown in Fig. 1. The Treanor distribution corresponds to  $r = 0$ .

V-T collisions dominate V-V exchange in the upper vibrational levels because of the large V-T probabilities in these levels. This upper level deactivation prevents the storage of vibrational energy and precludes the artificially high inversion predicted by Eq. (16) in high vibrational levels.

At low vibrational levels where the V-T probabilities are insignificant relative to the V-V probabilities, the distribution follows that of Treanor et al up to the minimum of the latter distribution. Beyond this point, it can be seen in Fig. 2 that the distribution behaves as  $vN_v =$  constant up to vibrational levels where V-T deactivation is important. From that point on, the distribution reverts to a Boltzmann distribution at the translational temperature.

The characteristic shape of the distribution function can be explained quantitatively. The constant  $vN_v$  behavior is due to the fact that, for the conditions and V-V probabilities chosen, near resonant collisions are far more effective in the transfer of vibrational quanta than nonresonant collisions. Thus, energy must be transferred up the vibrational ladder by near resonant collisions rather than go directly from the source in the first vibrational level to the deactivation region. Beyond the region of the Treanor minimum, the quanta flux supplied by the source can only be delivered from level to level by collisions with molecules in lower levels, i.e. for any level  $v + 1$  beyond the Treanor minimum:

$$\sum_{i=1}^v P_{i,i-1}^{v,v+1} N_v N_i \approx K \quad (17)$$

where the dominant contribution to the sum comes from levels close to  $v$ .

By the use of the Landau-Teller relations it follows that this is satisfied by

$$\sqrt{v(v+1)} N_v = \text{constant} \left( 1 + O\left(\frac{1}{v^2}\right) \right) \quad (18)$$

in agreement with the numerical calculations. This result is only valid up to the deactivation region. The region of strong V-T deactivation occurs when the net particle flux cannot maintain the constant  $vN_v$  slope to supply the local deactivation. A representative term in the flux then becomes  $P_{v,v-1}^{v,v+1} N_v^2 - P_{v-1,v}^{v+1,v} N_{v+1} N_{v-1}$  and by use of the Landau-Teller selection rules one finds that the deactivation occurs near level  $v'$  such that

$$\frac{P_{v',v'-1}^{v',v'+1}}{P_{1,0}^{1,2}} = v' \left( \frac{vN_v}{N_0} \right) e^{-2 \omega_e x_e hc/kT} \quad (19)$$

The value of  $vN_v$  is approximately that at the minimum of the Treanor distribution so that  $v'$  may be obtained in terms of the assumed probability distributions. Although the particle flux has been underestimated in choosing only one term of the sum, the resultant value for  $v'$  is quite accurate because of the rapid variation of the V-T probability with vibrational level as shown in Fig. 1.

The quanta source,  $K$ , necessary to maintain  $\Theta_1^*$ , is found to be constant for the different V-T probabilities assumed for the calculations. This is to be expected since there is no direct communication between the source and the deactivation region, and the only requirement on the

source is that it maintain the temperature in the lowest levels. Thus the source requirement will not increase until V-T probabilities are sufficiently large to affect the distribution in the lowest levels. It should be emphasized that these conclusions regarding the limitation to the quanta flux and the constant  $\nu N_v$  region are only applicable to situations in which near resonant collisions dominate. In fact, it is shown later that these calculations are invalid if the effective V-V collisional exchange is due to nonresonant collisions with low level molecules.

Figure 3 shows vibrational distribution calculations for a wide range of translational temperatures at the fixed value of  $\Theta_1^* = 2700^\circ\text{K}$ . These calculations illustrate the effect of varying the relative magnitude of the near resonant to nonresonant V-V collisional processes. In the low level region controlled by detailed balancing, the population density of the higher levels decreases with increasing translational temperature as seen in Eq. (16). The typical resonant collisional terms in the quanta flux behave like  $N_v^2 P_{v,v-1}^{v,v+1}$  whilst the nonresonant collisions with molecules in the lowest levels vary as  $N_v N_1 P_{1,0}^{v,v+1}$ . Thus for high vibrational levels, the collisions with the more densely populated lower levels become more important with increasing translational temperature. This effect is enhanced by the increase in the ratio of nonresonant to near resonant probabilities with increasing translational temperature.

The results for the three lowest translational temperatures all indicate a region of constant  $\nu N_v$  implying that the distribution beyond the Treanor minimum is dominated by near resonant V-V collisional exchange. However, at the higher translational temperatures the nonresonant

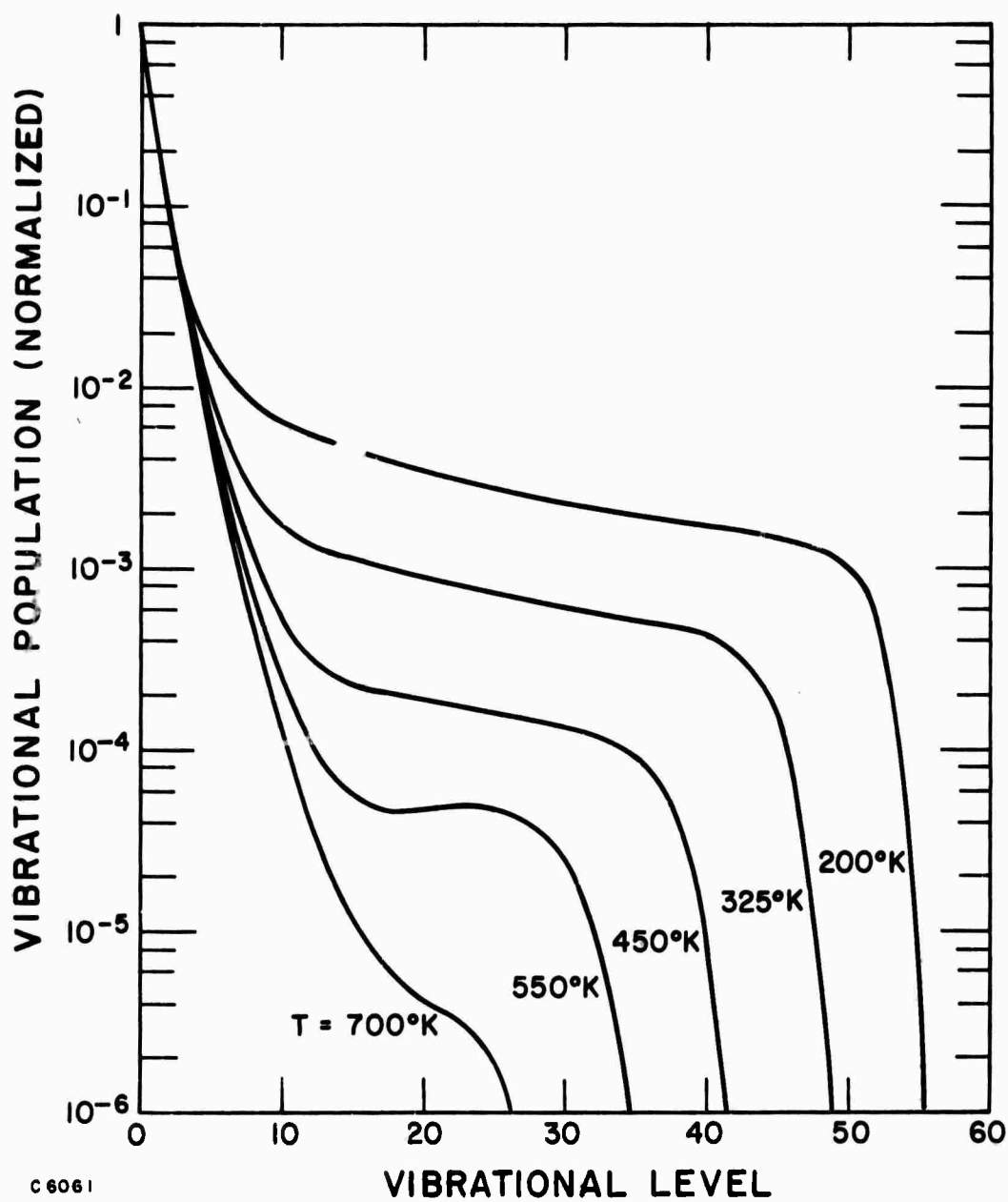


Fig. 3 CO vibrational distribution functions, neglecting radiative decay, for  $\theta_1^* = 2700^\circ\text{K}$  and for various translational temperatures.

collisions become more important resulting in a total vibrational inversion at 550°K. Since the V-T probability increases with the translational temperature, collisional deactivation prevents a total inversion in the distribution at 700°K.

The possibility of a total inversion can be readily demonstrated when nonresonant collisions dominate i. e. when the most effective V-V collisions are those with the highly populated low vibrational levels. In this case the leading term in the particle flux between levels  $v$  and  $v+1$  is

$$F_{v,v+1} \approx P_{1,0}^{v,v+1} N_v N_1 - P_{0,1}^{v+1,v} N_{v+1} N_0$$

and this is equal to the local drain which is approximately  $P_{V-T}^{v+1,v} N_{v+1}$ .

It follows that

$$\frac{N_v}{N_{v+1}} \approx \frac{P_{V-T}^{v+1,v}}{N_1 P_{1,0}^{v,v+1}} + \exp \left( \frac{E_1 - E_0}{k \Theta_1} - 2v \omega_e x_e \frac{hc}{kT} \right) \quad (20)$$

For vibrational levels beyond the Treanor minimum, the above expression predicts a total inversion up to vibrational levels where  $P_{V-T}^{v+1,v} / N_1 P_{1,0}^{v,v+1}$  is  $O(1)$ . The approximations in the above derivation are invalid near the region of the Treanor minimum because of errors resulting from small differences.

The fact that the present calculations for CO have predicted a small total inversion for only a very limited range of temperature conditions is related to the form of the V-V probability distribution used. It is obvious that a reduction in the variation of  $P_{1,0}^{v,v+1}$  with  $v$  will tend to favor the nonresonant collisions and should lead to a large inversion.



This is verified by the results in Fig. 4 where we have used the artificial probability distributions as shown which vary the ratio of near resonant to nonresonant probabilities. A strong inversion is evident at 325° translational temperature for the flat V-V probability distribution. Even for these artificial probability distributions near resonant collisions are important in the high vibrational levels. Thus the source is not linearly related to the drain and the inversion is limited by the V-V probability distribution. It should be emphasized that the V-V probabilities shown in Fig. 1 are in good agreement both in absolute magnitude and  $v$  dependence with the recent experimental data of Hancock and Smith.<sup>12</sup> Bray's calculations of quasi steady state distributions in  $N_2$ <sup>2</sup> also predict a total inversion after the minimum of the Treanor distribution for a range of values of  $\Theta_1^*/T$ . He assumed an approximate analytic variation of the V-V probabilities with vibrational level which is much flatter than the present probability distribution in CO.

#### B. T-V and Radiative Decay in Pure CO

Whereas the collisional exchange of energy between the vibrational and translational degrees of freedom is most significant at the higher vibrational levels, the decay of vibrational energy due to radiation is effective in all vibrational levels for an optically thin gas. In the present calculations the gas is assumed to be optically thin for all vibrational-rotational radiative transitions. This is valid in CO for pressures  $\lesssim 0.1$  Torr at room temperature over a characteristic length of 1 cm for trapping of radiation. These conditions are typical of the electrically pumped CO lasers. The results of these calculations are relatively

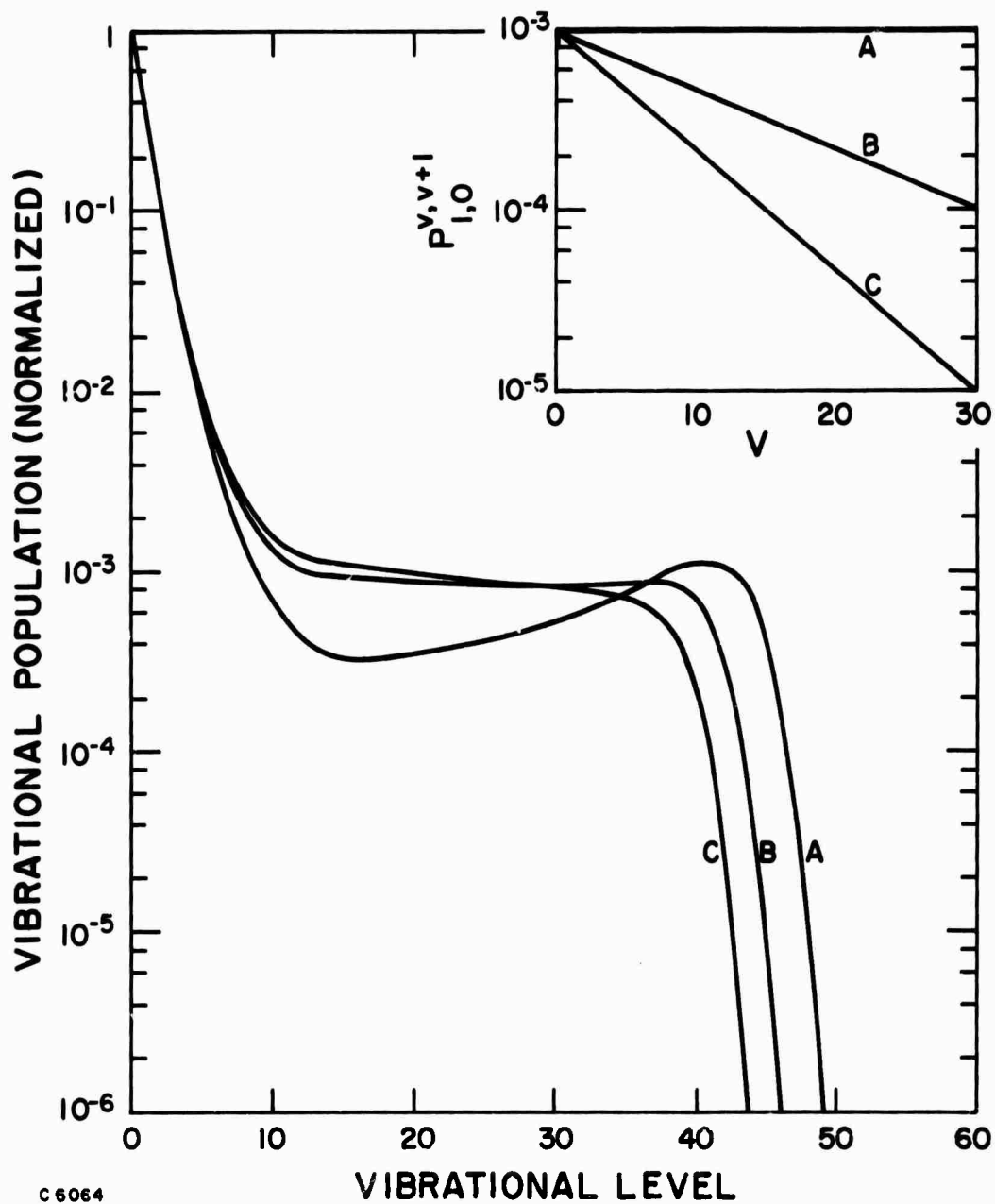


Fig. 4 CO vibrational distribution functions, neglecting radiative decay, for  $\Theta_1^* = 2700^\circ\text{K}$ ,  $T = 325^\circ\text{K}$  and the artificial V-V probability distributions as shown. The V-T probability distribution used is that shown in Fig. 1.

insensitive to optical opacity in the first few vibrational levels because the population distribution is controlled by the fixed vibrational temperature  $\Theta_1^*$ .

At low pressure, the radiation term in the master equation (6) becomes the dominant decay term. The effect of the radiative vs. V-T deactivation is shown in Fig. 5 as a function of the CO pressure. For the assumed conditions the distribution is controlled by radiative decay at pressures of the order of 0.1 Torr or less. Because of the distributed drain in energy due to the radiative decay, the slope of the vibrational distribution no longer varies linearly with  $v^{-1}$  after the minimum of the Treanor distribution.

The slope of the distribution in the high levels can be determined from particle flux considerations. At low pressures where the radiative decay is the dominant deactivation mechanism, the component of the flux in the forward direction becomes significantly more important than that in the backward direction and it follows that

$$\frac{N_v}{N_{v+1}} \approx \frac{P_{\text{rad}}^{v+1,v}}{\sum_i N_i P_{i,i-1}^{v,v+1}} \quad (21)$$

where the sum may be evaluated using Eq. (16) for the first few levels. Nonresonant collisions are more effective than near resonant collisions because of the low population densities in these high vibrational levels. Thus the slope varies approximately inversely with  $P_{1,0}^{v,v+1}$ . It is evident from the above result that the high level population distribution depends critically on the assumed probability distribution when the radiation decay dominates.

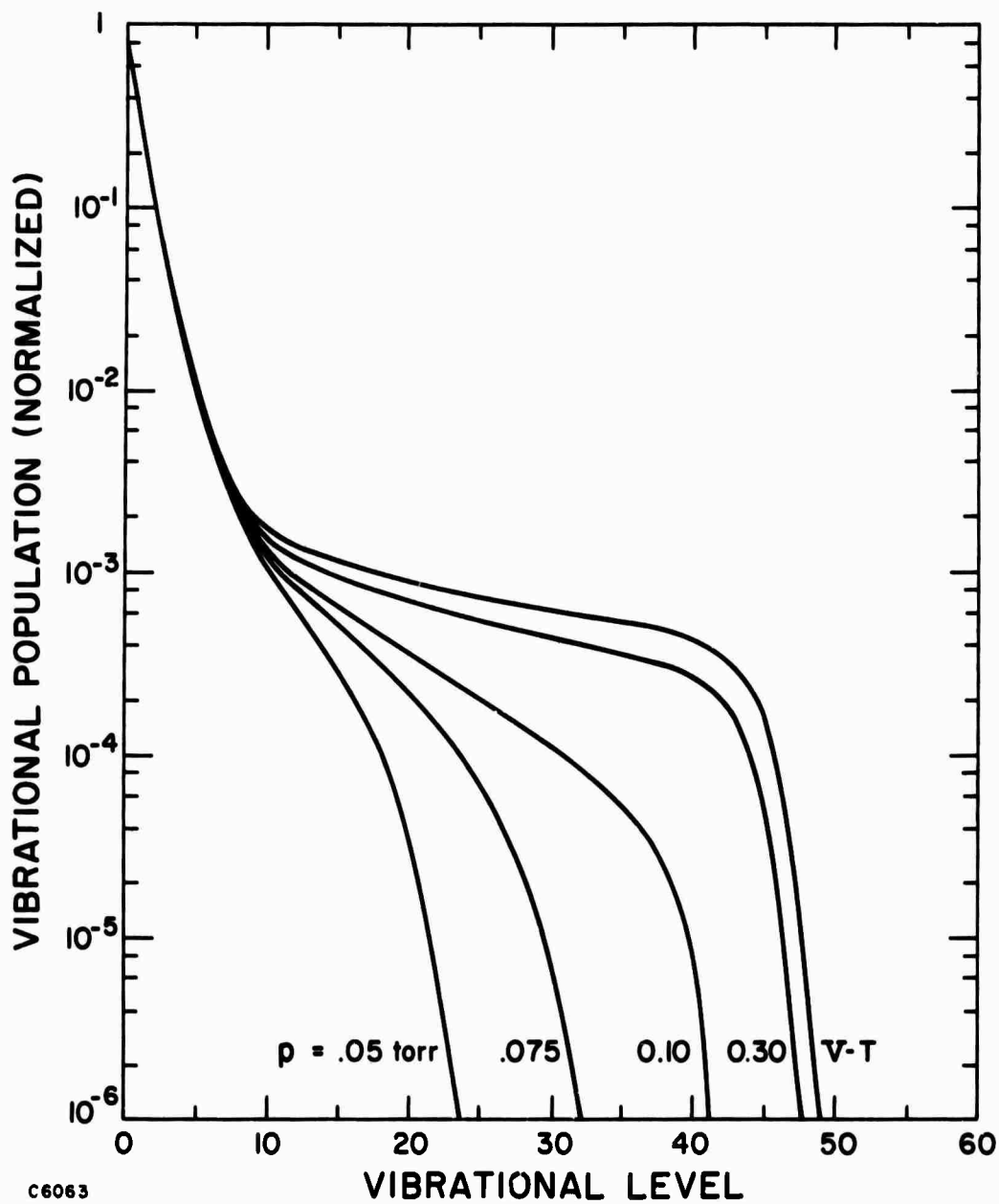


Fig. 5 The effect of radiative decay as a function of the CO pressure on the CO vibrational distribution functions for  $\Theta_1^* = 2700^\circ\text{K}$  and  $T = 325^\circ\text{K}$ . The curve labelled V-T would correspond to large CO pressures where radiative decay is unimportant.

### C. Calculations for N<sub>2</sub>: CO Mixtures

In the calculations discussed so far we have only considered pure CO and have determined the distribution for a fixed temperature,  $\Theta_1^*$ , in the lowest levels. Examples of the more general case in which the source communicates with all vibrational levels are the N<sub>2</sub>-CO mixing experiments in which the CO is a trace species and the "active" N<sub>2</sub> acts as an infinite source of vibrational energy. For comparison with this case we have assumed a fixed N<sub>2</sub> vibrational distribution and calculated the steady state distribution in CO as a result of energy transfer from the N<sub>2</sub> to the CO with subsequent intramode energy exchange as described in the preceding sections.

Because of the large energy difference between the first vibrational levels of N<sub>2</sub> and CO, (188 cm<sup>-1</sup>), there is a considerable difference in their vibrational temperatures. For example, at a translational temperature of 325°K, the CO vibrational temperature of 2700°K may be maintained by a N<sub>2</sub> vibrational temperature of 1700°K according to Eq. (10). As a result of this low N<sub>2</sub> vibrational temperature, there is far less intramode pumping of vibrational quanta in N<sub>2</sub> than in CO. Thus, the N<sub>2</sub> vibrational distribution is quite close to a Boltzmann distribution at  $\Theta_1^* = 1700^\circ\text{K}$ , 99% of the molecules and 92% of the vibrational quanta being in the first three levels. Therefore, the results are relatively insensitive to the high level N<sub>2</sub> distribution. For the present calculations we have used a Treanor distribution up to its minimum, this distribution being necessary to maintain V-V equilibrium between the anharmonic oscillators,<sup>1</sup> followed by a constant population density in the high levels of N<sub>2</sub>.

In Fig. 6 a comparison is made between the vibrational distribution calculated for 0.1 Torr pure CO and a mixture of  $N_2$ :CO with partial pressures of 2.0 Torr and 0.1 Torr, respectively. In the pure CO case a vibrational temperature of  $2700^\circ K$  was chosen for the lowest vibrational levels whilst the mixture calculations assume a  $N_2$  distribution which would pump CO to a temperature of  $2700^\circ K$  in the absence of any energy drain. In the mixture calculations, collisional communication is allowed between all levels of  $N_2$  and CO. The mixture calculation leads to a vibrational distribution which is only slightly lower than the distribution in pure CO except at the high vibrational levels where the intramode pumping cannot keep up with the V-T energy loss.

There are two basic reasons for the difference between the two distributions. Firstly, the V-T deactivation in the high levels is larger than for the pure CO calculations because of the large  $N_2$  fraction. For the present calculations we have assumed that the probability of V-T deactivation of CO by  $N_2$  is the same as for CO by CO as expected theoretically. To verify the effect of this increased V-T drain, we have repeated the pure CO calculation with the V-T rate increased by the mole fraction ratio. The result is shown in Fig. 6 and the effect of higher V-T rates is only evident at high levels. Secondly, the assumed  $N_2$  vibrational temperature was obtained from the pumping formula (10) without taking the energy loss mechanism into account. It is this small but finite energy loss which reduces the population distribution and the vibrational temperature  $\Theta_1^*$  at the lower vibrational levels. Thus to achieve a particular

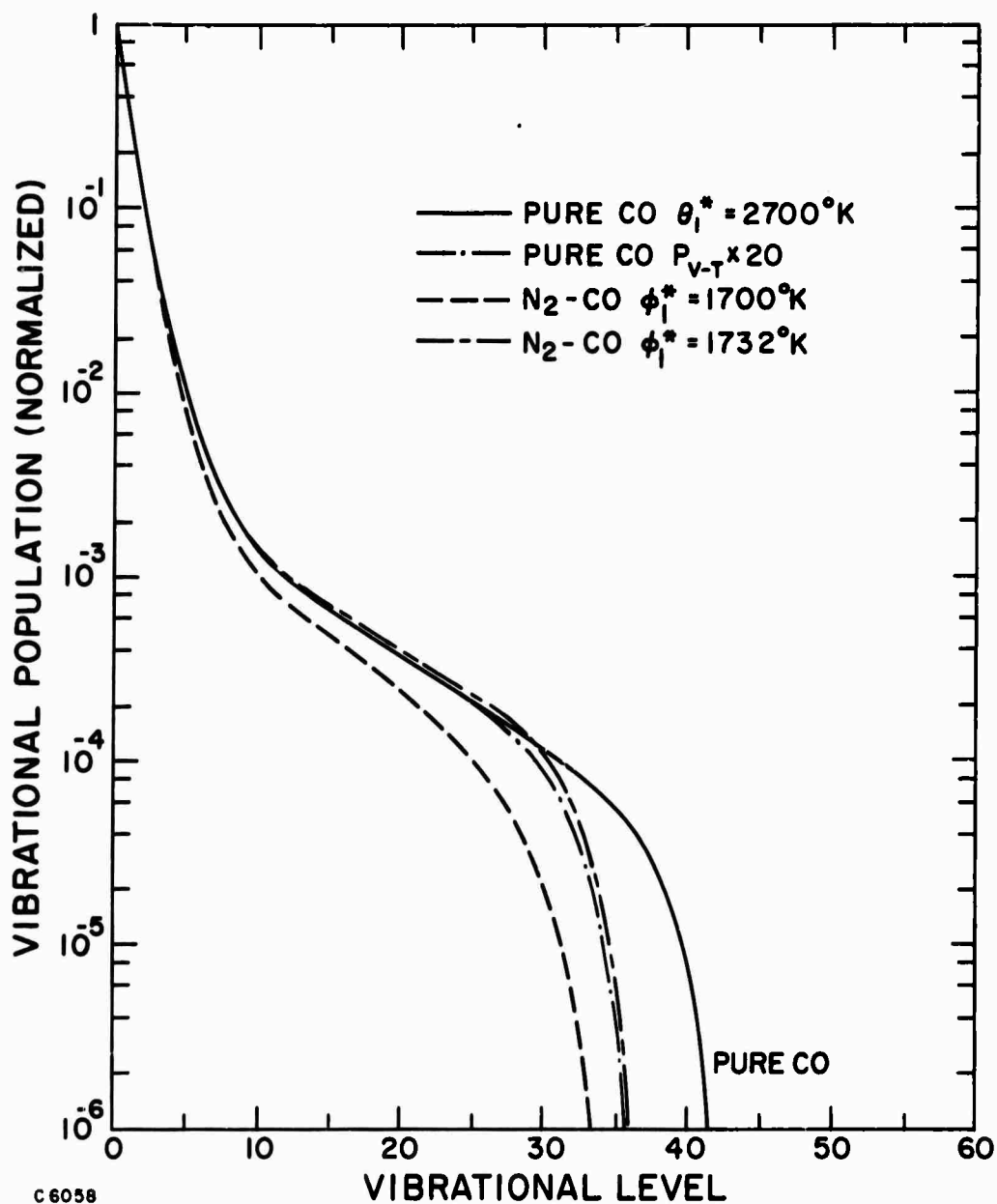


Fig. 6 CO vibrational distribution functions for N<sub>2</sub>-CO mixtures with a fixed N<sub>2</sub> distribution.  $\phi_1^*$  is the vibrational temperature between the zeroth and first levels of the N<sub>2</sub> distribution. The partial pressures of CO and N<sub>2</sub> are 0.1 and 2.0 Torr, respectively, and  $T = 325^\circ\text{K}$ .

vibrational temperature in the lowest levels of CO requires an  $N_2$  vibrational temperature somewhat higher than predicted by Eq. (10).

For a harmonic oscillator model one can readily estimate the correction to the  $N_2$  vibrational temperature as a function of the ratio  $\tau_{V-V}/\tau_{rad}$  when radiation is the dominant loss mechanism. This correction can be obtained from the energy relaxation Eq. (9). For time scales short compared to the V-T relaxation time, one can set the last two terms of Eq. (9) equal to zero in the steady state approximation. This is in agreement with the underlying concept in this work that the redistribution of vibrational energy occurs in time scales much shorter than the collisional deactivation, i. e.  $\tau_{V-V} \ll \tau_{V-T}$ . Then one can derive the following relationship for the  $N_2$  vibrational temperature in terms of the small parameter  $\epsilon = \tau_{V-V}/\psi_{N_2} \tau_{rad}$  and the required vibrational temperature in CO

$$\frac{\theta_{CO}}{T_{VCO}} - \frac{\theta_{N_2}}{T_{VN_2}} + \frac{\theta_{N_2} - \theta_{CO}}{T} = \ln \left\{ 1 + \epsilon (1 - e^{-\theta_{N_2}/T_{VN_2}}) \right\} \quad (22)$$

For the sample calculation shown in Fig. 6 the correction to the  $N_2$  vibrational temperature amounts to some 30°K. The corrected CO distribution is shown in Fig. 6 and is within a few percent of the pure CO distribution except for  $v > 30$  where the increased V-T deactivation is important as described above.

It is evident from the similarity of the pure CO and mixture calculations, presented in Fig. 6, that the vibrational levels of  $N_2$  communicate predominantly with the first vibrational level of CO for



the chosen conditions and rates. This is due to the vibrational energy defect for transitions between the low levels of  $N_2$  and higher levels in CO. The energy defect increases with vibrational level in CO. Conversely the higher levels of  $N_2$  become more nearly resonant with the  $v=1 \rightarrow v=0$  transition of CO and resonance occurs between the sixth and seventh levels of  $N_2$  and the first and zeroth level of CO. Mixture calculations made with the restriction that the  $N_2$  communicate only with the first and zeroth levels of CO agreed to within a few percent with the complete communication calculation for the assumed V-V rates. It should be noted that a sufficiently large increase in the  $N_2$ -CO V-V rate would result in an increase in the high level population densities in CO as a result of some direct communication with the low levels in  $N_2$ . However, a decrease in V-V rate with suitable correction to the  $N_2$  temperature by means of Eq. (22) would not change the CO distribution since the  $N_2$  would then only communicate with the lowest levels of CO.

Thus, the mixture calculations show that for typical  $N_2$ -CO mixtures the distribution in CO is characterized mainly by the low level temperature  $\Theta_1^*$ . The nonresonance in the V-V energy exchange between  $N_2$  and CO results in the CO intramode exchange being much faster than the effective intermode exchange when corrected by the mole fraction ratio.

#### Comparison with Experimental Data

The currently available experimental data for the vibrational distribution in CO have been obtained in electrical  $N_2$ -CO mixing experiments. The  $N_2$  is first made vibrationally active by passage

through a RF discharge and subsequently undergoes V-V collisional exchange with CO which is mixed in small concentrations into the  $N_2$  stream. In the experiments by Joeckle<sup>15</sup> and by Horn and Oettinger,<sup>17</sup> the vibrational distribution in the CO is derived from the overtone emission spectrum. Legay<sup>18</sup> obtained data for the vibrational distribution from  $v=7$  to  $v=17$  from gain measurements in an electrical  $N_2$ -CO mixing laser. In order to compare the experimental results with the steady state predictions, it must be assumed that quasi V-V equilibrium has been reached in the experiment. This was experimentally verified by Horn and Oettinger and is almost certainly true in the other two experiments in which the time after mixing is long compared with the CO V-V relaxation time.

All the calculations for comparison with the experimental vibrational distribution data have been obtained for pure CO with the appropriate  $\Theta_1^*$  and due allowance made for the increased V-T deactivation due to the  $N_2$ . The pure CO calculation is justified in view of the mixture calculations in the preceding section which were made for similar mixtures of  $N_2$  and CO. Furthermore, it is assumed that metastable electronic states in the excited  $N_2$  play no role in the excitation of the CO. Figure 7 shows a comparison of the experimental data of Joeckle and the numerical results. Since  $\Theta_1^*$  is not measured in the experiment, we have chosen  $\Theta_1^*$  to provide the best fit of a Treanor distribution with the low level data making use of the experimentally determined translational temperature. Two numerical results are shown, the second being derived with twice the nominal V-V probability

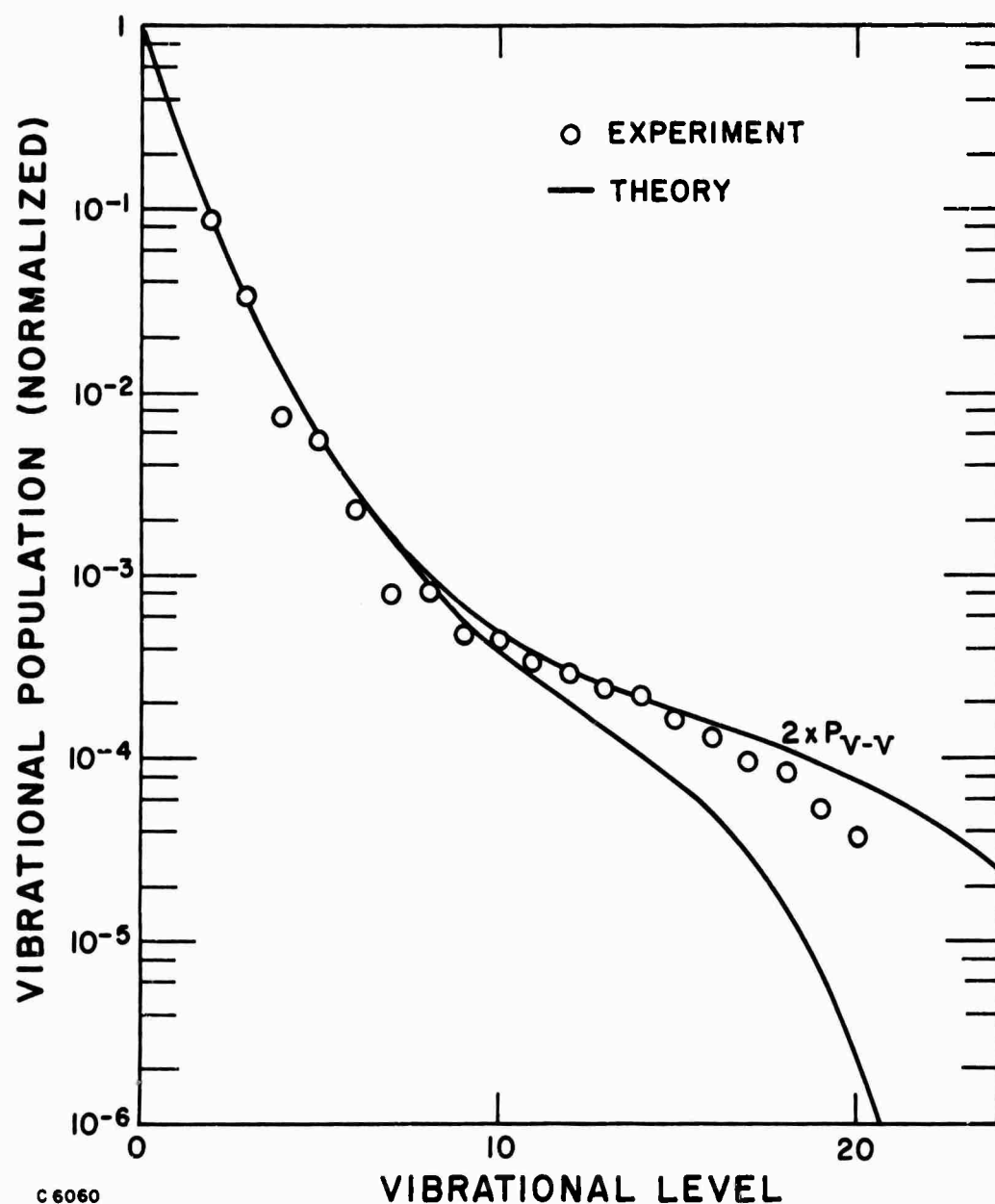


Fig. 7 Comparison of experimental CO distribution (Ref. 15) with calculations for  $\Theta_1^* = 2500^\circ\text{K}$ ,  $T = 350^\circ\text{K}$  and  $p_{\text{CO}} = 0.08$  Torr. The upper theoretical curve illustrates the effect of increasing the V-V probabilities by a factor of 2.

to demonstrate the sensitivity of low pressure data to the V-V rates. It is evident from the master equation that a change in the magnitude of the V-V probabilities is equivalent to a change in the CO pressure by the same amount. This can be significant at low pressures when the radiative decay is the dominant loss mechanism as in the present results.

The data of Horn and Oettinger are shown in Fig. 8 and correspond to lower pressures in CO and much higher vibrational temperatures. The numerical calculations have been made for two values of  $\Theta_1^*$  for each pressure, the lower value corresponding to that determined by Horn and Oettinger in curve fitting a Treanor distribution to the first four vibrational levels. Their values of  $\Theta_1^*$  are a lower estimate because of the low level deactivation due to the strong effect of radiative decay at the low pressures. This underestimate of  $\Theta_1^*$  is evident in the improved fit of the data for the calculations at the higher values of  $\Theta_1^*$ . These higher values of  $\Theta_1^*$  were chosen to demonstrate the effect of low level radiative decay and are not necessarily the optimum values. The sensitivity of the calculations to the V-V probabilities is somewhat less than in the comparison in Fig. 7 because of the higher values of  $\Theta_1^*$ . The experiment at  $\Theta_1^* = 3500^\circ\text{K}$  has the largest mole fraction ratio and the highest  $\text{N}_2$  temperature, approximately  $2060^\circ\text{K}$  in the lowest levels, of all the data considered. A mixture calculation for this extreme case agreed with the pure CO distribution calculation in the lower levels and was less than a factor of two larger in the higher levels.

Finally, we have the comparison with the measurements by Legay presented in Fig. 9. These measurements were made at a much higher

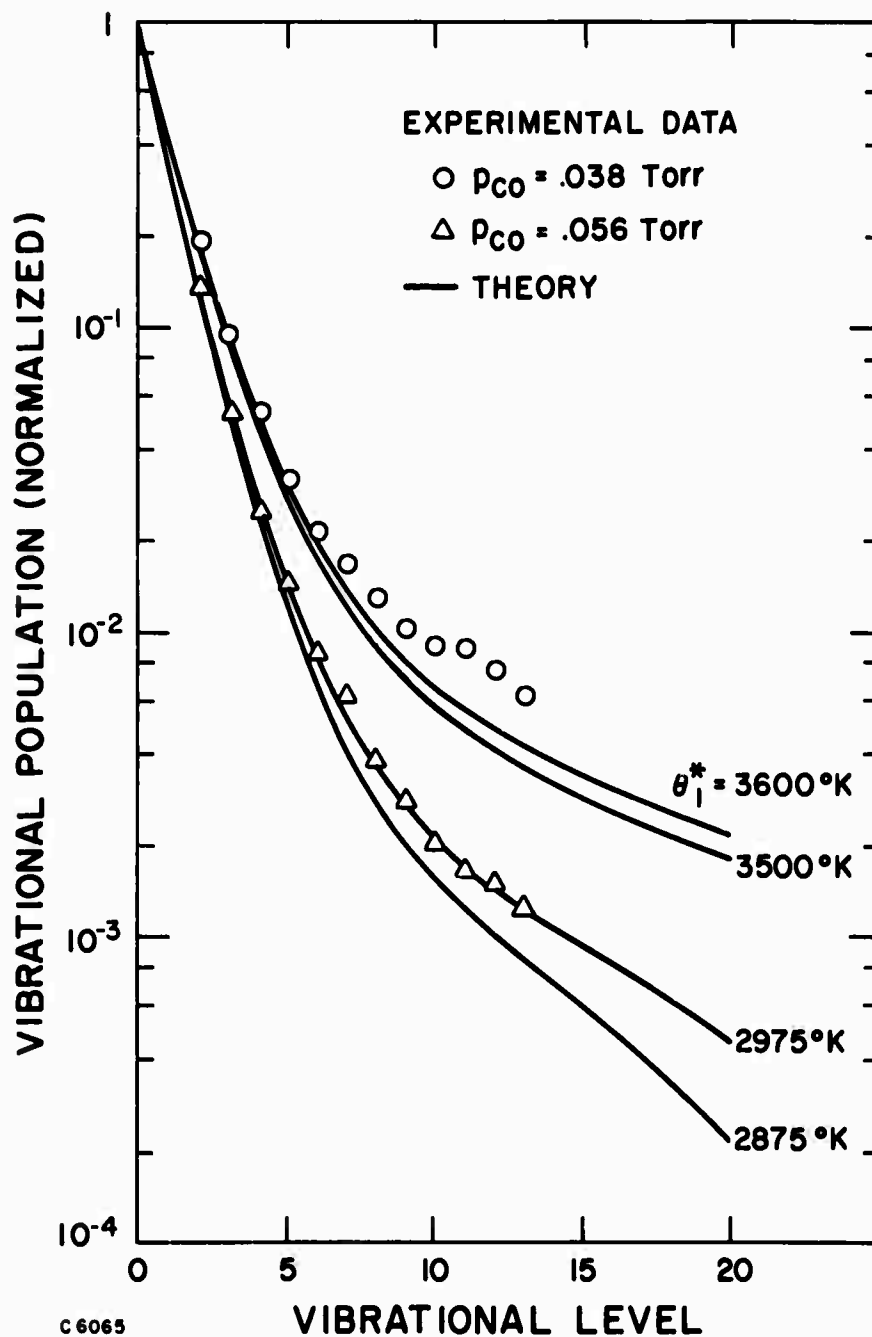


Fig. 8 Comparison of experimental CO distribution (Ref. 17) with calculations for  $T = 350^\circ K$ . The lower curves are for values of  $\theta_1^*$  deduced in Ref. 17, and the upper curves show the effect of a small variation in  $\theta_1^*$ .

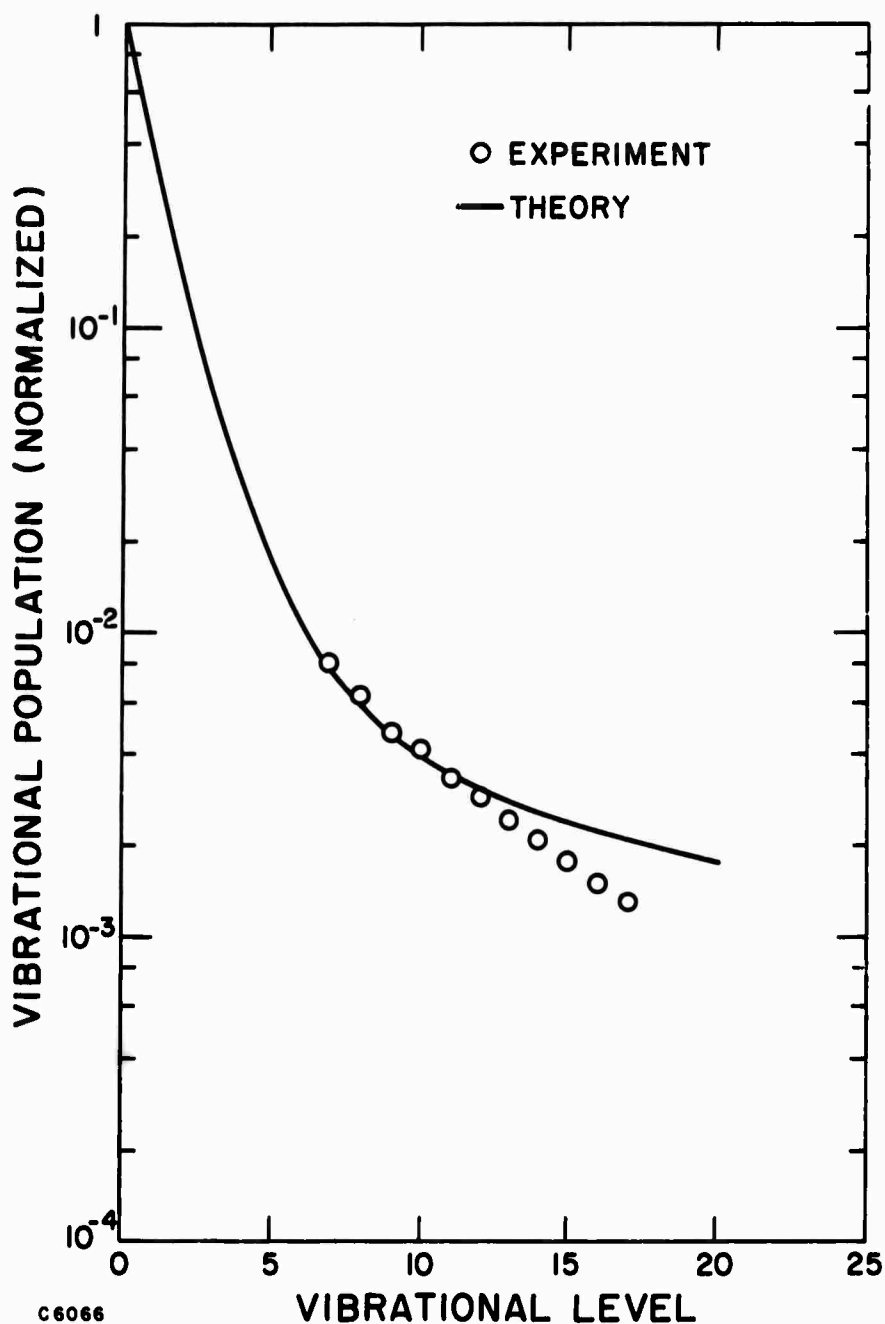


Fig. 9 CO distribution calculation compared with the experimental data of Ref. 18 for  $\Theta_1^* = 3000^\circ\text{K}$ ,  $T = 325^\circ\text{K}$  and  $p_{\text{CO}} = 0.3$  Torr. The experimental data are limited to  $v \geq 7$  as they were deduced from gain measurements in a  $\text{N}_2$ -CO laser which only operated above  $v=6$ .

CO pressure than the previous data and the calculations do not predict the high level decay which was observed experimentally. Although there is a possible large error in the estimated value of  $\Theta_1^*$ , this will not greatly affect the high level population density variation because radiative effects are expected to be relatively small at 0.3 Torr as indicated in Fig. 5. There is no obvious explanation for the discrepancy between theory and experiment at the high vibrational levels. One possible reason for the apparent discrepancy in the high level data is the deactivation of these levels by  $O_2$  which is present in the laser to maintain an equilibrium concentration in CO. The high vibrational levels in CO are resonant with the  $v=1$  to  $v=0$  transition in  $O_2$ . The experimental technique may also result in small inconsistencies in the data because it requires separate gain measurements for each pair of vibrational levels unlike the overtone spectrum which encompasses all vibrational levels. A reduction in the V-V rates would reduce the high level population, but this reduction is not suggested by the comparison with the other experimental data. It is also possible that the high level V-T probabilities have been underestimated in the present calculations.

We believe that the comparisons shown in Figs. 7 to 9 indicate reasonable agreement of the experimental data with the analytic model of vibrational energy transfer in CO and  $N_2$ -CO mixtures.

#### IV. CONCLUSION

A model has been developed to calculate the steady state vibrational distribution of a diatomic gas under conditions of thermal nonequilibrium. Calculations have been made for the case of a binary gas mixture with one gas acting as an infinite source of energy for the other. It is shown that under suitable conditions the distributions may be well approximated by the assumption that the source of energy which maintains the distribution communicates only with the zeroth and first vibrational level. The model can readily be extended to predict the distributions in a binary mixture excited by an external source.<sup>19</sup> An example of interest is the directly excited  $N_2$ -CO laser. The calculations include both collisional deactivation and radiative decay to account for the energy loss from the system. These decay processes prevent a large inversion in the upper vibrational levels which might otherwise occur as a result of intramode vibrational energy pumping due to the molecular anharmonicity. It is shown that radiative decay may be the dominant loss mechanism in low pressure  $N_2$ -CO experiments.

The numerical calculations are found to be in reasonably good agreement with the available experimental data all of which have been obtained in electrically excited  $N_2$ -CO mixing systems. It is evident from the comparison with the experimental data that more detailed kinetic rate information is needed particularly for the high level collisional deactivation processes. Within that limitation the present model



gives a satisfactory account of the experimentally observed non Boltzmann distributions based solely on collisional exchange of vibrational energy and radiative decay.

On the basis of existing theories for the probability of collisional exchange, it would appear that near resonant intramode pumping will be an important if not the dominant mechanism for energy pumping. When near resonant collisions are the dominant intramode pumping mechanism, it has been shown that a total inversion is not possible unless the source can communicate directly with high vibrational levels by intermode pumping.

Under conditions where the near resonant collisions dominate and radiative decay is not important, some simple criteria have been derived to predict the distribution function. These predictions are based on knowledge of the translational temperature and the low level vibrational temperature which are more readily accessible to experimental measurement than the high level distributions. Similar prediction criteria have been derived for the case when radiative decay is the dominant energy loss.

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